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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 2004OPA3005	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. **PCT/KR2004/000887**	International filing date *(day/month/year)* **16 APRIL 2004 (16.04.2004)**	Priority date *(day/month/year)* 17 APRIL 2003 (17.04.2003)
International Patent Classification (IPC) or national classification and IPC **IPC7 B82B 3/00**		
Applicant **KYUNGWON ENTERPRISE CO., LTD. et al**		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ (sent to the applicant and to the International Bureau) a total of 7 sheets, as follows:
      - ☒ sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      - ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.

   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) ____________, containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:
   - ☒ Box No. I Basis of the report
   - ☐ Box No. II Priority
   - ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - ☐ Box No. IV Lack of unity of invention
   - ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - ☐ Box No. VI Certain documents cited
   - ☐ Box No. VII Certain defects in the international application
   - ☐ Box No. VIII Certain observations on the international application

Date of submission of the demamd **16 NOVEMBER 2004 (16.11.2004)**	Date of completion of this report 05 AUGUST 2005 (05.08.2005)
Name and mailing address of the IPEA/KR Korean Intellectual Property Office 920 Dunsan-dong, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, SI GEUN Telephone No. 82-42-481-8151

Form PCT/IPEA/409 (cover sheet) (January 2004)

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/KR2004/000887

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
   - [x] This report is based on translations from the original language into the following language English which is the language of a translation furnished for the purposes of:
     - [ ] international search (under Rules 12.3 and 23.1(b))
     - [x] publication of the international application (under Rule 12.4)
     - [ ] international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this reort as "originally filed" and are not annexed to this report):*
   - [ ] the international application as originally filed/furnished
   - [x] the description:
     pages 1, 2, 5, 6 and 9 - 12 as originally filed/furnished
     pages* 3, 4,, 7, 8-1 and 8-2 received by this Authority on 16 November 2004
     pages* ____ received by this Authority on ____
   - [x] the claims:
     pages 15 ____
     pages* ____ as originally filed/furnished
     pages* 13 and 14 as amended (together with any statment) under Article 19
     pages* ____ received by this Authority on 16 November 2004
     pages* ____ received by this Authority on ____
   - [x] the drawings:
     pages 1/7 - 7/7 ____
     pages* ____ as originally filed/furnished
     pages* ____ received by this Authority on ____
     pages* ____ received by this Authority on ____
   - [ ] the sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. [ ] The amendments have resulted in the cancellation of:
   - [ ] the description, pages ____
   - [ ] the claims, Nos. ____
   - [ ] the drawings, sheets ____
   - [ ] the sequence listing *(specify)* : ____
   - [ ] any table(s) related to sequence listing *(specify)* : ____

4. [ ] This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - [ ] the description, pages ____
   - [ ] the claims, Nos. ____
   - [ ] the drawings, sheets ____
   - [ ] the sequence listing *(specify)*: ____
   - [ ] any table(s) related to sequence listing *(specify)* : ____

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/KR2004/000887

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1 - 19	YES
	Claims		NO
Inventive step (IS)	Claims	1 - 19	YES
	Claims		NO
Industrial applicability (IA)	Claims	1 - 19	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

The following documents have been considered for the purpose of this report:

D1 = US 6,387,531 B1
D2 = KR 2002-37428 A

The present invention relates to a 3-dimensional nano-structured metal-carbon composite characterized in being prepared using a nano template and containing chemical bonds of metal-carbon and a method for preparing the same. In the method of the invention, metal precursor and carbon precursor is mixed in a nanoplate, the reaction mixture produced therefrom is carbonized and then, said nanotemplate is removed.

D1 relates to the nanocomposites of carbon and metal oxide, not the nanocomposites of carbon and metal. D2 relates to a method of manufacturing a porous alumina nanotemplate and a method of manufacturing carbon nanotube in said nanotemplate.

I. Novelty and Inventive Step

The 3-dimensional nano-structured metal-carbon composite characterized in being prepared using a nano template and containing chemical bonds of metal-carbon, and the method of manufacturing a nano-structured metal-carbon composite by mixing metal precursor and carbon precursor in a nano template, carbonizing and removing the nano template of claims 1-19 are not considered to be easily invented from the invention disclosed in D1 and D2 by a person skilled in the art.

II. Industrial Applicability

There is no reason for forming a negative opinion about the industrial applicability of this invention. Consequently, claims 1 - 19 appear to meet the requirement of PCT Article 33(4).

carbon nano-tube for hydrogen storage (J. Mat. Chem. 2003, 13, 209).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Technical Subject

The object of the present invention is to solve the above-described problems, namely- to provide a nano-structured metal-carbon composite which may combine a transition metal such as platinum to a mesoporous carbon having a porous nano-structure other than fullerene or carbon nano-tube in a simple and economical manner, easily change an electronic structure of the carbon and have excellent hydrogen storage capacity at room temperature, and a method for preparation thereof.

Technical Solution

In order to achieve the above-described object, a 3-dimensional nano-structured metal-carbon composite containing chemical bonds of metal-carbon is manufactured using a nano template. Here, the nano template is selected from silica oxide, alumina oxide or mixtures thereof, preferably, a silica oxide.

In the nano-structured metal-carbon composite of the present invention, a carbon precursor of the metal-carbon composite is selected from the group consisting of furfuryl alcohol, glucose and sucrose. Preferably, the carbon precursor is sucrose.

In the nano-structured metal-carbon composite of the present invention, the metal-carbon composite comprises at least one metal selected from the group consisting of Pt, Ru, Cu, Ni, Mg, Co, W, Fe, Ir, Rh, Ag, Au, Os, Cr, Mo, V, Ta, Zr, Hf, Li, Na, K, Be, Ca, Ba, Mn, Pd, Ti, Zn, Al, Ga, Sn, Pb, Sb, Se, Te, Cs, Rb, Sr, Ce, Pr, Nd, Sm, Re and B. Further, the metal precursor is selected from $(NH_3)_4Pt(NO_3)_2$, $(NH_3)_6RuCl_3$, $CuCl_2$, $Ni(NO_3)_2$, $Mg(NO_3)_2$, $CoCl_2$, $(NH_4)_6W_{12}O_{39}$, $FeCl_3$ or $FeCl_3(NH_4)_3$, $IrCl_6$, $RhCl_3$, $AgCl$, NH_4AuCl_4, $OsCl_3$, $CrCl_2$, $MoCl_5$, VCl_3, $TaCl_5$, $ZrCl_4$, $HfCl_4$, Li_2CO_3, $NaCl$, KCl, $Be(CH_3COCHCOCH_3)_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $Pd(NO_3)_2$, $TiCl_4$, $ZnCl_2$, $AlCl_3$, Ga_2Cl_4, $SnCl_4$, $PbCl_2$, $SbCl_3$, $SeCl_4$, $TeCl_4$, $CsCl$, $RbCl$, $SrCl_2$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $ReCl_3$ and BCl_3.

In the nano-structured metal-carbon composite of the present invention, the metal is contained in an amount ranging from 1 to 95wt% and the carbon is contained in an amount ranging from 5 to 99wt%, based on the gross weight of the metal-carbon composite. Preferably, the metal is contained in an amount ranging from 4 to 36wt% and the carbon is contained in an amount ranging from 64 to 96wt%, based on the gross weight of the metal-carbon composite.

In the nano-structured metal-carbon composite of the present invention, the platinum is contained in an amount ranging from 0.2 to 44wt% and the carbon is contained in an amount ranging from 56 to 99.8wt%, based on the gross weight of the

metal-carbon composite. Preferably, the platinum is contained in an amount ranging from 2 to 34wt% and the carbon is contained in an amount ranging from 66 to 98wt%, based on the gross weight of the metal-carbon composite.

In an embodiment, a process for preparing a 3-dimensional nano-structured metal-carbon composite containing chemical bonds of metal-carbon comprises:

the preparation step of preparing a nano template;

the calcination step of calcining the prepared nano template;

the impregnation step of impregnating a metal into the calcined nano template using a metal precursor;

the addition and mixing step of adding a carbon precursor in the nano template impregnated with the metal and mixing the carbon precursor uniformly;

the reaction step of reacting the resultant mixture prepared in the addition and mixing step;

the carbonization step of carbonizing the resultant reacted mixture; and

the removal step of removing the nano template from the resultant carbonized mixture.

In the method according to the present invention, the nano template is selected from silica oxide, alumina oxide or mixtures thereof, and preferably, the nano template is a silica oxide.

In the method according to the present invention, the reaction step is performed at a temperature ranging from 100 to 160°C, and the carbonization step is performed at a temperature ranging from 800 to 1000°C.

In the method according to the present invention, the carbon precursor is selected from the group consisting of furfuryl alcohol, glucose and sucrose. Preferably, the carbon precursor is sucrose.

In the method according to the present invention, the metal-carbon composite comprises at least one metal selected from the group consisting of Pt, Ru, Cu, Ni, Mg, Co, W, Fe, Ir, Rh, Ag, Au, Os, Cr, Mo, V, Ta, Zr, Hf, Li, Na, K, Be, Ca, Ba, Mn, Pd, Ti, Zn, Al, Ga, Sn, Pb, Sb, Se, Te, Cs, Rb, Sr, Ce, Pr, Nd, Sm, Re and B, and the metal precursor is selected from $(NH_3)_4Pt(NO_3)_2$, $(NH_3)_6RuCl_3$, $CuCl_2$, $Ni(NO_3)_2$, $Mg(NO_3)_2$, $CoCl_2$, $(NH_4)_6W_{12}O_{39}$, $FeCl_3$ or $FeCl_3(NH_4)_3$, $IrCl_6$, $RhCl_3$, $AgCl$, NH_4AuCl_4, $OsCl_3$, $CrCl_2$, $MoCl_5$, VCl_3, $TaCl_5$, $ZrCl_4$, $HfCl_4$, Li_2CO_3, $NaCl$, KCl, $Be(CH_3COCHCOCH_3)_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $Pd(NO_3)_2$, $TiCl_4$, $ZnCl_2$, $AlCl_3$, Ga_2Cl_4, $SnCl_4$, $PbCl_2$, $SbCl_3$, $SeCl_4$, $TeCl_4$, $CsCl$, $RbCl$, $SrCl_2$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $ReCl_3$ and BCl_3.

The disclosed nano-structured metal-carbon composite according to the present invention is prepared using a nano template. For the nano template used in Examples 1 to 7, SBA-15 of a silica oxide type has been primarily used but MCM-48 of a silica oxide

160°C respectively for 6 hours, and carbonized under a vacuum atmosphere at 900°C. The nano template was melt and removed with diluted fluoric acid aqueous solution, and washed, thereby obtaining a nano-structured Pt-C composite.

Examples 2 to 45

Preparation of nano-structured metal-carbon composite using nano template

After the nano template (SBA-15) obtained from Example 1 was calcined at 300°C, a mixture impregnated with 24wt% Ru, Cu, Ni, Mg, Co and W respectively based on the 1g of the nano template was prepared using a vacuum drier. For precursors of Ru, Cu, Ni, Mg, Co and W, $(NH_3)_6RuCl_3$, $CuCl_2$, $Ni(No_3)_2$, $Mg(NO_3)_2$, $CoCl_2$, $(NH_4)_6W_{12}O_{39}$ were used respectively. Thereafter, sucrose (2.5g), sulphuric acid (0.28g) and water (10g) were added to the resultant mixture and mixed uniformly. Then, the resultant mixture was reacted at 100°C and 160°C respectively for 6 hours, and carbonized under a vacuum atmosphere at 900°C. The nano template was melt and removed with diluted fluoric acid aqueous solution, and washed, thereby a nano-structured ruthenium-carbon composite (Example 2), a copper-carbon composite (Example 3), a nickel-carbon composite (Example 4), a magnesium-carbon composite (Example 5), a cobalt-carbon composite (Example 6) and a tungsten-carbon composite (Example 7).

The following analysis experiment was performed to find the structure of the nano-structured platinum-carbon composite (Example 1) prepared using a nano template.

In order to analyze the structure of the nano-structured platinum-carbon composite, a Transmission Electron Microscope (TEM), a X-ray Diffractometer (XRD), a pore analyzer, an Extended X-ray Absorption Fine Structure (EXAFS) were used.

Fig. 1 shows an observation result of the nano-structured platinum-carbon composite obtained from Example 1 using the TEM. As shown in Fig. 1, the disclosed nano-structured metal-carbon composite was observed to have a 3-dimensional structure.

Fig. 2 is a XRD analysis result of the nano-structured platinum-carbon composite obtained from Example 1. Since the XRD analysis result of the disclosed nano-structured metal-carbon composite was the same as that of SBA-15, the disclosed composite was observed to have a replica fabricated as a shape of the nano template. This experimental result supports the fact that the nano-structured platinum-carbon composite has a 3-dimensional structure.

Fig. 3 is a pore structure analysis result of the nano-structured platinum-carbon composite obtained from Example 1. Fig. 3 shows that the disclosed composite has a great deal of fine pores consisting of micro-pores of less than 1 nano-meter and mesopores. As a result of calculation with adsorption isotherm, the BET surface area is observed to be almost $1700m^2/g$.

Fig. 4 shows EXAFS analysis results of the nano-structured platinum-carbon

composite obtained from Example 1 and those of the conventional platinum-carbon composite. The curves A and D show a result of the disclosed platinum-carbon composite, and the curves B and C show a result of the conventional composite.

More specifically, the curve A of Fig. 4 shows an analysis result of the platinum-carbon composite obtained from Example 1, and the curve D shows an analysis result of the platinum-carbon composite obtained from Example 1 which was subsequently treated with bromine mixed solution (*Microporous and Mesoporous* Mat. 31, 23-31 (1999)) so that platinum was present only in micro-pores of less than 1 nano-meter.

Also, the curve B shows a result using a platinum-carbon composite obtained by dispersing commercial Vulcan carbon in dilute H_2PtCl_6 solution, dehydrating the resultant mixture with an evaporating drier and then reducing the resultant mixture under a hydrogen atmosphere at 310°C. Although the curve C has the same procedure as that of the curve B, the curve C shows a result of a platinum-carbon composite using mesoporous carbon obtained by carbonizing only a carbon precursor in a nano template (*J. Am. Chem. Soc.* 122, 10712-10713 (2000)) instead of Vulcan carbon.

Table 1 shows a graph simulation result of EXAFS from the analysis result of Fig. 4.

[Table 1] Graph simulation result of EXAFS

	Sample	Pt-Pt bond number	Pt-C bond number	Pt-Pt bond length (nm)	Pt-C bond length (nm)
A	Nano-structured Pt-C Composite (1)	4.31	2.73	0.2735	0.2041
B	Pt/C (1)	9.58		0.2757	
C	Pt/C (2)	9.71		0.2757	
D	Nano-structured Pt-C Composite (2)	2.78	2.12	0.2736	0.2014

As shown in Table 1, the Pt-C bond number and length could be determined in the nano-structured Pt-C composite (1) and the nano-structured Pt-C composite (2) (corresponding to the curves A and D of the analysis result of Fig. 4, respectively) while

the Pt-C bond number and length could not be determined in the conventional Pt/C (1) and Pt/C (2) (corresponding to the curves B and C of the analysis result of Fig. 4, respectively). It is clear from the above results that metal and carbon are simply mixed in the conventional composites, while metal and carbon are not simply mixed but platinum of less than 1 nano-meter and carbon are chemically bonded in the disclosed nano-structured Pt-C composite. That is, it is precisely known that the disclosed composite has a novel chemical bond structure even in less than 1 nano meter fine micro-pores. Accordingly, the stable chemical bond of metal and carbon represents a novel characteristic structure of the disclosed nano-structured Pt-C composite.

Although carbon is a stable material in general, the carbon may be used as a useful material if the structural characteristic is changed as shown in the present invention. Since the disclosed nano-structured metal-carbon composite using a nano template may combine various metals chemically, the carbon included in the composite exhibits various characteristics. For example, if some metal is introduced into a catalyst to regulate a band gap, it is probable to generate hydrogen through split of water. Since power consumption can be reduced using a metal-carbon composite having excellent conductibility in a manufacture process of semiconductor elements, the disclosed composite may be used in a fine element process. Furthermore, since carbon can

What is Claimed is:

1. A 3-dimensional nano-structured metal-carbon composite characterized in being prepared using a nano template and containing chemical bonds of metal-carbon.

2. The nano-structured metal-carbon composite according to claim 1, wherein the nano template is selected from silica oxide, alumina oxide or mixtures thereof.

3. The nano-structured metal-carbon composite according to claim 2, wherein the nano template is a silica oxide.

4. The nano-structured metal-carbon composite according to claim 1, wherein a carbon precursor of the metal-carbon composite is selected from the group consisting of furfuryl alcohol, glucose and sucrose.

5. The nano-structured metal-carbon composite according to claim 4, wherein the carbon precursor is sucrose.

6. The nano-structured metal-carbon composite according to one of claims 1 to 5, wherein the metal-carbon composite comprises at least one metal selected from the group consisting of Pt, Ru, Cu, Ni, Mg, Co, W, Fe, Ir, Rh, Ag, Au, Os, Cr, Mo, V, Ta, Zr, Hf, Li, Na, K, Be, Ca, Ba, Mn, Pd, Ti, Zn, Al, Ga, Sn, Pb, Sb, Se, Te, Cs, Rb, Sr, Ce, Pr, Nd, Sm, Re and B.

7. The nano-structured metal-carbon composite according to claim 6, wherein the metal precursor is selected from $(NH_3)_4Pt(NO_3)_2$, $(NH_3)_6RuCl_3$, $CuCl_2$, $Ni(NO_3)_2$, $Mg(NO_3)_2$, $CoCl_2$, $(NH_4)_6W_{12}O_{39}$, $FeCl_3$ or $FeCl_3(NH_4)_3$, $IrCl_6$, $RhCl_3$, $AgCl$, NH_4AuCl_4, $OsCl_3$, $CrCl_2$, $MoCl_5$, VCl_3, $TaCl_5$, $ZrCl_4$, $HfCl_4$, Li_2CO_3, $NaCl$, KCl, $Be(CH_3COCHCOCH_3)_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $Pd(NO_3)_2$, $TiCl_4$, $ZnCl_2$, $AlCl_3$, Ga_2Cl_4, $SnCl_4$, $PbCl_2$, $SbCl_3$, $SeCl_4$, $TeCl_4$, $CsCl$, $RbCl$, $SrCl_2$, $CeCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $ReCl_3$ and BCl_3.

8. The nano-structured metal-carbon composite according to one of claims 1 to 7, wherein the metal is contained in an amount ranging from 1 to 95wt% and the carbon is contained in an amount ranging from 5 to 99wt%, based on the gross weight of the metal-carbon composite.

9. The nano-structured metal-carbon composite according to claim 8, wherein the metal is contained in an amount ranging from 4 to 36wt% and the carbon is contained in an amount ranging from 64 to 96wt%, based on the gross weight of the metal-carbon composite.

10. The nano-structured metal-carbon composite according to claim 6 or 7, wherein the platinum is contained in an amount ranging from 0.2 to 44wt% and the carbon is contained in an amount ranging from 56 to 99.8wt%, based on the gross weight of the metal-carbon composite.

11. The nano-structured metal-carbon composite according to claim 10, wherein the platinum is contained in an amount ranging from 2 to 34wt% and the carbon is contained in an amount ranging from 66 to 98wt%, based on the gross weight of the metal-carbon composite.

12. (Amended) A process for preparing a 3-dimensional nano-structured metal-carbon composite containing chemical bonds of metal-carbon, comprising:

the preparation step of preparing a nano template;

the calcination step of calcining the prepared nano template;

the impregnation step of impregnating a metal into the calcined nano template using a metal precursor;

the addition and mixing step of adding a carbon precursor in the nano template impregnated with the metal and mixing the carbon precursor uniformly;

the reaction step of reacting the resultant mixture prepared in the addition and mixing step;

the carbonization step of carbonizing the resultant reacted mixture; and

the removal step of removing the nano template from the resultant carbonized mixture.

13. The method according to claim 12, wherein the nano template is selected from silica oxide, alumina oxide or mixtures thereof.

14. The method according to claim 13, wherein the nano template is a silica oxide.

15. The method according to claim 12, wherein the reaction step is performed at a temperature ranging from 100 to 160°C, and the carbonization step is